

STATE OF SOUTH CAROLINA CERTIFICATION REQUIREMENTS FOR ORGANIC ANALYSES

In accordance with State Regulation 61-81, certification is required for all laboratories performing analyses to determine the quality of air, drinking water, hazardous waste, solid waste or wastewater required by or submitted to the South Carolina Department of Health and Environmental Control. Certification is presently offered under the Safe Drinking Water Act (SDWA), Clean Water Act (CWA) and Resource Conservation and Recovery Act (RCRA). Certification will also be offered as requested by the specific Program areas of SCDHEC for other analyses. Laboratories performing analyses for the organic contaminants must use only those methodologies approved by these regulations or specified by SCDHEC. Strict adherence to the approved methodology is a minimum requirement for certification under the South Carolina Laboratory Certification Program.

The EPA approved methodology for the Safe Drinking Water Act is referenced in 40 CFR Parts 141 and 142. The EPA Approved methodology for the Clean Water Act is referenced in 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act". The methodology approved for RCRA analyses is referenced in 40 CFR Part 261 along with specified methodology in "SW-846, Test Methods for Evaluating Solid Wastes, Physical and Chemical Methods" required by SCDHEC.

To obtain certification under the South Carolina Certification Program the following documentation for organic analyses must be submitted in addition to the completed application and application fee prior to scheduling an on-site laboratory evaluation:

- 1) Standard Operating Procedures and Quality Assurance Manual.
- 2) Initial demonstration of capability for each analyte and method that the laboratory is seeking certification to perform. This data must include a laboratory reagent water blank and at least four replicate analyses with each analyte of concern at the concentration specified in the method. Applicable cleanup procedures if used must be included with this initial demonstration of capability.
- 3) Multi-level calibration documentation for each analyte by each method that the laboratory is seeking certification to perform.
- 4) Method detection limit study for each analyte by each method according to the procedure in Appendix B of 40 CFR Part 136 (Must be performed on an annual basis).
- 5) Acceptable results with the supporting documentation for applicable "unknown" performance evaluation samples obtained from an approved commercial vendor. For SDWA certification EPA Water Supply Performance Evaluation Studies will be used to meet the specified performance criteria. Approval for the regulated VOCs under the SDWA is based on analyzing 80% of the regulated VOCs correctly. Vinyl chloride must be analyzed with acceptable results.

For each day these analyses are performed the method specified quality control such as laboratory reagent water blanks, quality control check samples, surrogates and calibration standards must be documented. The supporting documentation such as extraction and cleanup records, instrument calibration records, analysis records, chromatograms and data system reports must be submitted for review. For gas chromatograph methodology, the requested documentation must also be submitted for the confirmation column or detector employed.

Quality Assurance Plan

All certified laboratories must adhere to defined quality assurance procedures, therefore insuring that routinely generated analytical data are scientifically valid and defensible and are of known and acceptable precision and accuracy. Each laboratory must prepare a written description of its quality assurance practices (QA plan). The following items must be addressed in the quality assurance plan.

- 1) Field sampling procedures:
 - Equipment
 - Sampling procedures
 - Instrument calibration
 - Field analysis and instrumentation
- 2) Sample handling procedures to maintain sample integrity:
 - Sample preservation
 - Sample custody
 - Sample control procedures and chain of custody
 - Sample identification
 - Record keeping and storage
- 3) Instrument or equipment calibration procedures and frequency of their use:
 - Standard source
 - Comparability checks
 - Multiple point
 - Frequency
 - Documentation
- 4) Analytical procedures:
 - Biological
 - Inorganic
 - Organic
 - Radiological
 - Microbiological
- 5) Data reduction, validation and reporting:
 - Calculations-dilution/concentration
 - Conversion of raw data to ug/l, mg/l, mg/kg, etc
 - Validation
 - Accuracy of data transcription and calculations
 - Reporting criteria for data integrity
 - Significant figures, procedures and formats for reporting data to regulatory officials
 - Required documentation
- 6) Field and laboratory quality control checks:
 - Field quality control:
 - Equipment blanks

- Field blanks
- Trip blanks
- Field Duplicates
- Laboratory quality control:
- Preparation of calibration curves
- Instrument calibrations
- Laboratory reagent blanks
- Replicate analyses
- Check sample recoveries
- Surrogate recoveries
- Matrix spike recoveries
- Instrument control standard response
- Internal standard response
- Control charts
- Documentation

7) Preventive maintenance schedules and procedures:

- Operating Manuals
- Instrument and equipment maintenance
- Routine maintenance
- Preventive maintenance schedule
- Spare parts inventory
- Service agreements
- Contingency plan
- Documentation

8) Specific routine procedures used to determine precision and accuracy for each contaminant measured:

- Measure of variability
- Statistical terms
- Control charts
- Corrective actions
- QA reports to the management
- Employee Training
- Laboratory Safety
- Timeliness
- Legibility/Clarity

9) Corrective action contingencies:

- QC sample failure(Laboratory reagent blanks, spikes, surrogates, etc.)
- PE sample failure
- Audit deficiency
- Customer complaint

The Quality Assurance Plan may be a separately prepared document or it may consist of standard operating procedures (SOP's) which are approved by the laboratory director and address the above items. Some items may not be relevant to all laboratories, in this case the QA plan should state this and provide a brief explanation. The QA plan must be tailored to a laboratory's operations. All quality assurance data must be readily available for review by the Laboratory Certification Program.

Standard Operating Procedures (SOPs)

Each certified environmental laboratory must have a Standard Operating Procedures (SOPs) Manual. The SOPs must be a detailed manual describing the operations of the laboratory for each parameter it is certified to perform. Each procedure must include the following information.

- 1) Scope and Application: Type of samples analyzed and the analytes of interest
- 2) Summary of the method: A brief explanation of the procedure.
- 3) Definitions: For inexperienced personnel define the terms used throughout the methodology.
- 4) Interferences: This would include contaminants from glassware, solvents, reagents, and other apparatus used in the laboratory. Matrix interferences contaminants coextracted from the sample. Unresolved peaks due to coelution.
- 5) Safety: List all safety items needed to perform the analysis as well as safety precautions needed.
- 6) Apparatus and equipment: List all apparatus and equipment needed to perform the test.
- 7) Reagents and consumable materials: Include manufacturer, catalog number and other pertinent information.
- 8) Sample preservation and handling: List specifics for each program area.
- 9) Calibration procedures and reagent standardizations: Standard I.D. numbers, amounts and concentrations must be specified. Calibration by a specific data system must be included.
- 10) Analytical procedures: This must include all procedures needed for the analysis for the contaminants of interest. For organic analyses this would include the extraction, cleanup, chromatography and identification procedure. Example chromatograms should be included for guidance.
- 11) Quality control: This must include field and laboratory quality control practices. These must be specific for each area of analysis and program area. Precision and accuracy requirements must be specified along with the quality control "start-up test". Frequency of quality control check samples.
- 12) Calculations: This section must describe the specific calculation used to determine the concentration of the method analyte. Specifics concerning the data system used must be included .

The Standard Operating Procedures must be updated at regular intervals by the laboratory and must be referenced to the EPA approved method. This manual must be made available to all personnel for training purposes.

Initial Demonstration of Capability

An initial demonstration of capability is required for each method and analyte that the laboratory is seeking certification to perform. The Laboratory Certification Program and the EPA refer to this as a quality

control "start-up test". The quality control "start-up test" is required for all methodology as an initial validation of the method and as a means to verify precision and accuracy of the analysts performing the methodology. The analyst is permitted to modify GC columns, GC detectors, GC operating conditions, continuous extraction techniques, concentration techniques, internal standards or surrogate compounds. Each time such method modifications are made the laboratory must repeat the quality control "start-up test" described in the method. This procedure is described in detail in the 600 and 1600 series methodology in section 8 and is used in the Drinking Water 500 series methods and the SW-846 Solid Waste Methods.

The Quality Control "start-up test" consists of an analysis of four replicate analyses with the pollutants of interest spiked into reagent water at a concentration specified in the method. If the method does not specify a concentration, the laboratory is to use a concentration at 5 to 10 times the detection limit for the method. The laboratory is required to perform this procedure prior to practicing the method and the results of the "start-up test" must be submitted to the Laboratory Certification Section for initial approval. Records of the "start-up test" must be available for each chemist participating in an analysis to demonstrate the required precision and accuracy. Use the enclosed form for documenting data for the quality control "start-up test".

For the four replicate determinations the mean recovery and the standard deviation between the four measurements is compared with method specified performance criteria. If either of the precision or accuracy test fails, the test must be repeated until the laboratory is able to meet the precision and accuracy requirements. For PCBs the quality control "start-up test" can be performed on an early and late eluting PCB instead of performing it on all the PCBs.

The quality control "start-up test" is required for all new analysts whether they are extraction analysts or the analysts performing the instrumental analyses to ensure that each analyst can meet the method specified accuracy and precision. The quality control "start-up test" must also be repeated when the laboratory modifies a method. The laboratory must demonstrate that the accuracy and precision specifications can be met with the modification otherwise the modification is not permitted. This documentation must be maintained on file in the laboratory. If cleanup steps are employed the accuracy and precision of this technique must be demonstrated through the same quality control "start-up test".

As mentioned earlier if a change is made to a method the quality control "start-up test" must be repeated with the change as an integral part of the method. These changes may include an alternate extraction apparatus, concentration technique, alternate columns, GC conditions or detectors and added cleanup processes or other steps designed to address a particular matrix problem. If the quality control "start-up test" is not repeated when these steps are modified or added all data produced by the modified method are considered not valid.

If there is no record of the quality control "start-up test" data or if these data fail to meet the specifications in the method all data produced by that laboratory using that method are considered invalid. Performing the quality control "start-up test" after the fact is not acceptable and may not be used in an attempt to validate data that have been considered not valid because the "start-up test" was not performed.

Quality Control

The laboratory must operate a formal quality control program and maintain records to document the quality of the data that is generated. The following quality control practices are considered minimum requirements for certification:

- 1) A laboratory reagent water blank must be included with each analytical batch of sample processed.
- 2) A laboratory control sample (LCS) or laboratory fortified blank (LFB) must be included with each analytical batch of samples processed and at least one every twenty samples. The LCS or LFB is a spiked reagent water blank.

- 3) A surrogate(s) must be added to all standards and samples with the results included with the analytical data.
- 4) A laboratory must spike and analyze a minimum of 10% of the samples except for some GC/MS analyses which allow 5% of the samples to be spiked.
- 5) A laboratory must duplicate at least 10% of the samples analyzed.
- 6) Trip blanks must accompany each set of volatile organic samples.
- 7) Continuing calibration checks must be performed at the beginning and end of an analysis sequence and every tenth sample analyzed meeting the method specified performance criteria.
- 8) Quality control check samples must be analyzed on a quarterly basis for each analyte and method that the laboratory is certified to perform.

Some methods contain additional quality control requirements that must also be included in the quality control program. These include but are not limited to verifying the GC/MS tune with BFB or DFTPP, analyzing a laboratory performance check solution or documenting endrin and p,p'DDT breakdown. If the method requires additional quality control practices these must be documented. All quality assurance data must be readily available for review by the Laboratory Certification Section.

Accuracy and precision data must be compiled by the laboratory with control limits established and updated periodically. These control limits are to be established for the laboratory control samples, matrix spikes, duplicates, surrogates and quality control check samples. Control limits must be documented with the analytical results.

Laboratories must successfully analyze an "unknown" performance evaluation sample annually for those contaminants for which audits are available. The EPA's Water Pollution Study is used for certification of Clean Water Act and Solid and Hazardous Waste parameters and the EPA's Water Supply Study is used for the Safe Drinking Water Act parameters. These studies consist of an initial study (even number) and a follow-up study (odd number). When unacceptable results are obtained the follow-up performance evaluation study is to be analyzed for only those parameters with unacceptable results. The only exception would be for the Water Supply Study for which acceptable performance is based on the group of regulated VOCs therefore the entire group of VOCs must be reanalyzed.

Organic Record Keeping Requirements

Appropriate documentation must be maintained for all quality control practices and analyses performed by the laboratory. Without this required documentation the data would not be legally defensible.

1. General Analysis Records

The laboratory must maintain the following information for all analyses performed under State Regulation 61-81. All records must be in ink and initialed or signed. Information may be retained electronically if a hard copy is verified by the analyst or the Laboratory Director.

- 1) Date and time of analysis
- 2) Analyst performing the analysis
- 3) Analytical method employed
- 4) Unique laboratory sample I.D. number
- 5) Raw data generated by the analysis and the results

- 6) All quality control data including standards, blanks, spikes, duplicates, blanks, surrogates, trip blanks, etc.
- 7) Formulas used for calculating test results along with an example identifying all terms in the equation
- 8) Reference to the calibration curve used to generate results or data table for linear regression analyses
- 9) All instrument operating conditions
- 10) Notations for unusual samples or other comments warranted are to be recorded.

When subcontracting analyses to another laboratory, a copy of the report from the originating laboratory must be retained on file. It is the responsibility of the laboratory to ensure that the contracted laboratory is certified for all analyses requested.

2. Quality Control Start-up Documentation

When submitting the data, include all extraction or sample preparation records, instrument operating conditions, instrument calibration data, analysis records, chromatograms, data system printouts and any other pertinent information. Reagent water blank analysis, a calibration check analysis and any other quality control practices required by the method employed must be submitted with all Quality control start-up data. For gas chromatograph methods Quality control start-up documentation must be provided for both the primary column and the confirmation column.

3. Method Detection Limit Study Documentation

The supporting data that must be submitted will include all extraction or sample preparation records, instrument operating conditions, instrument calibration data, analysis records, chromatograms, data system printouts and any other pertinent information. Reagent water blank analysis, a calibration check analysis and any other quality control practices required by the method employed must be submitted with all MDL studies performed. For gas chromatograph methods MDL studies must be provided for both the primary column and the confirmation column.

4. Sample Preparation or Extraction Records

Sample preparation or extraction records must be maintained for any analysis conducted by the laboratory performed under Regulation 61-81. This record must contain the following items as warranted by the method employed.

- 1) Method Number
- 2) Date and time of sample preparation or extraction
- 3) Unique sample I.D. number
- 4) Extraction or sample preparation technique
- 5) Extraction or sample preparation solvent
- 6) Volume or weight of sample used (include dry weight and wet weight of sample)
- 7) Sample preparation analyst
- 8) I.D. number of surrogate spiking mixture with concentration and volume added
- 9) I.D. number of spiking mixture with concentration and volume added
- 10) Sample clean-up and/or derivatization method employed
- 11) Date and time sample clean-up or derivatization employed
- 12) Clean-up/derivatization analyst
- 13) Final volume of extract and solvent
- 14) Comments

Some laboratories use a logbook to record sample preparation as a batch or have a separate sample preparation record for each sample. The instrument operator must be provided with a copy of the extraction or sample preparation records to be able to associate blanks, spikes and duplicates with the appropriate batch of samples. Laboratories must have a system in place by which blanks, matrix spikes and duplicates are designated. The instrument operator must also know the sample volume or weight prepared or extracted along with the final volume of sample submitted for analysis.

5. Instrument Calibration Records

Instrument calibration records must document the following:

- 1) Method
- 2) Date and time for each calibration standard analyzed
- 3) Instrument and detector I.D.
- 4) Instrument operating conditions
- 5) Column I.D.
- 6) Compilation of area responses versus concentration for each analyte
- 7) Mean calibration factor, standard deviation, and the percent relative standard deviation for each analyte if using a calibration factor
- 8) When using a calibration curve the slope, y-intercept and the correlation coefficient must be recorded for each analyte.
- 9) Analyst's initials. Each analyst must prepare their own calibration curve.

The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. Weekly at least one standard at the concentration of the reporting limit for each analyte must be analyzed to verify instrument response.

The frequency of calibration verification is dependent on the detector and types of samples analyzed. The electron capture detector is more susceptible to changes in detector response caused by GC column and sample effects, therefore, more frequent calibration checks must be performed. On the other hand the flame ionization detector is much less sensitive and requires less frequent verification.

When verifying the working calibration curve or calibration factor the response for the calibration check standard must not vary by more than a specified amount from the predicted response or a new calibration curve must be regenerated. The percent difference must be calculated each time the calibration curve or calibration factor is verified.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

Several of the methods specify the use of a Q.C. check sample to verify instrument calibration. When using these methods a Q.C. check sample must be used in place of the calibration standards. The Q.C. check sample must be from a source independent from the

stock solution used to prepare the calibration standards. In the methods specifying the Q.C. check sample, the results must meet the acceptance criteria "Q" as given in the applicable method.

EPA Methods 601, 602, 603, and 624 specify the use of a Q.C. check sample to verify instrument calibration.

6. Instrumental Analysis Records

Instrumental analysis records must be maintained for all analyses performed under State Regulation 61-81. This includes instrument calibration, reagent water blank analyses, matrix spike and duplicate analyses, quality control measurements performed throughout an analysis period. The following information must be documented for each sample analyzed:

- 1) Method number
- 2) Instrument I.D.
- 3) Instrument operator with date of analysis
- 4) Detector
- 5) Analytical Column
- 6) Instrument operating conditions
- 7) Daily GC/MS Performance test results
- 8) Daily instrument calibration check results
- 9) Sample I.D. number
- 10) Volume of sample purged or injected
- 11) Extract volume of sample injected
- 12) I.D. number of internal standard material
- 13) Dilutions if performed
- 14) Confirmations required

Some laboratories combine this record with the sample preparation and extraction record. Many laboratories keep these separate in a logbook maintained by the analyst on a daily basis.

7. Chromatograms and Data System Reports

Chromatograms and data system reports must be kept together or at least labeled appropriately in order to distinguish which data system report goes with which chromatogram. The following information must be documented on these reports:

- 1) Method employed
- 2) Date and time of analysis
- 3) Instrument I.D.
- 4) Analyst
- 5) Analytical column
- 6) Attenuation
- 7) Unique Sample I.D. number
- 8) Sample volume purged or injected
- 9) Extract volume injected from
- 10) Date of referenced calibration curve (include slope and y-intercept)
- 11) Peaks must be labeled with retention time and contaminant I.D.
- 12) Calculations
- 13) Analytical results with the appropriate units

14) Confirmations needed

8. Chemical Inventory Record

All laboratories are to maintain a chemical inventory record by recording the following information for the standards, solvents and chemicals received by the laboratory.

- 1) Reference or identification number
- 2) Standard, solvent or chemical name
- 3) Vendor or manufacturer
- 4) Order or catalog number
- 5) Volume/weight
- 6) Lot number
- 7) Purity/concentration
- 8) Date received with initials
- 9) Storage location
- 10) Date opened and initials
- 11) Date of disposal and initials

This inventory record helps laboratories in estimating the use of certain standards, solvents and chemicals. All chemicals, standards and solvents are to be labeled with the date received and date opened.

9. Chromatography Column Inventory Record

The following information is to be recorded for the chromatography columns received in the laboratory.

- 1) Date of receipt
- 2) Column type: Packed or capillary
- 3) Column description: Stationary phase, length, ID, film thickness
- 4) Vendor or manufacturer
- 5) Catalog number
- 6) Date conditioned
- 7) Temperature conditioned
- 8) Date used and method
- 9) Column evaluation (include chromatogram)
- 10) Column Maintenance
- 11) Date discarded

10. Standard Preparation Record

All standard preparations are to be documented. Records can be differentiated by type of contaminant such as volatile, base/neutral or acid extractable, pesticide/PCB, herbicide, etc. Laboratories divide each of these groups into concentrated stock standards by weight, standard mixes by dilution, and standards by dilution. An index can be maintained on all standards prepared by the laboratory with the section and page number for easy reference by the analyst.

Each standard received or prepared by the laboratory is to be assigned a unique standard I.D. number and this number must be printed on the vial label for the standard material. This number is to be referenced in analysis records and on chromatograms in order to verify the correct preparation for the standard material and to ensure that it has not exceeded its

holding time.

11. Instrument Maintenance Record

An instrument maintenance record is to be kept on each instrument used for regulatory analyses. This would include all preventive and corrective maintenance. By keeping an instrument maintenance record, analysts will be able to consult these records for changes made to the instrumentation that could be related to a change in resolution or sensitivity. The analyst can also use this record for troubleshooting if a certain problem had been encountered before.

The types of items that need to be included in this record include but are not limited to replacing carrier gases, traps, columns, detectors, septums, injector inserts, and filaments. Maintenance and cleaning of the detectors or ion source. On a daily basis check column, detector, and injector temperature along with carrier gas pressure and carrier gas flow rate. If a change in retention time, resolution, or sensitivity is noted the analyst is to evaluate all instrument operating conditions to isolate and correct the problem. Always record the problem in the maintenance record and tell how the problem was corrected.

Major maintenance includes cleaning an ion source, cleaning quadrupole rods etc. which results in recalibration of the GC/MS. This will also include replacing the MS electron multiplier or any other faulty component.

A written log must be maintained on each instrument recording the following information.

- 1) Date of installation and serial number of each detector installed
- 2) Date of column installation and performance
- 3) Results of the column evaluation mixture
- 4) Chromatogram displaying optimum performance for the contaminants of interest
- 5) Chromatograms with special column evaluation mixtures
- 6) Documentation of column, septum or gas changes. This must include the repacking of the chromatographic column or replacing the glass wool. For capillary columns if the column is shortened or rinsed it must appear in the records.
- 7) For purge and trap apparatus, trap changes must be documented.
- 8) Any other maintenance performed on the gas chromatograph or gas chromatograph mass spectrometer by the laboratory analysts or by the authorized service representative.

Any major instrument modifications will result in the need to performed the required initial demonstration of the laboratory's capability. The Method Detection Limit study must also be repeated.